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## Binuclear Complexes of Transition Metals Containing Carbonate Ligands. Preparation, Properties, and Crystal Structure of $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$

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The reaction of a solution of  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] chloride and sodium bicarbonate at 40 °C resulted in the isolation of black needlelike crystals of  $\mu$ -amido- $\mu$ -hydroxo-tetraamminebis(carbonato)cobalt(III) pentahydrate. The complex has been characterized unambiguously by means of a three-dimensional X-ray diffraction study. The complex crystallizes in the monoclinic space group  $P2_1/c$  [ $C_{2h}^5$ ; No. 14] with  $a = 9.557$  (2) Å,  $b = 15.848$  (3) Å,  $c = 9.804$  (2) Å,  $\beta = 90.31$  (1) Å,  $V = 1484.8$  (5) Å<sup>3</sup>,  $\rho(\text{obsd}) = 1.864$  (13) g cm<sup>-3</sup>, and  $\rho(\text{calcd}) = 1.919$  g cm<sup>-3</sup> for  $Z = 4$  and mol wt 429.11. Diffraction data were collected on a Syntex  $P2_1$  automated four-circle diffractometer by using a coupled  $\theta$ - $2\theta$  scan and Mo  $K\alpha$  radiation. The structure was solved via direct methods and refined by difference Fourier and least-squares refinement techniques. The final discrepancy indices were  $R_F = 4.4\%$  and  $R_{wF} = 3.8\%$  for those 3435 total reflections in the range of  $3.5^\circ \leq 2\theta \leq 50.0^\circ$ . The cobalt(III) complex has the structure  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2$ —i.e., both of the incoming carbonate ligands are chelated to the same cobalt atom. The cobalt(III) ions are each in an octahedral coordination environment, the Co(1)---Co(2) distance being 2.862 (1) Å. Important bond distances are Co—( $\mu$ -OH) = 1.932 (3) and 1.908 (2) Å, Co—( $\mu$ -NH<sub>2</sub>) = 1.916 (3) and 1.899 (3) Å, Co—NH<sub>3</sub> = 1.960 (3)—1.986 (3) Å, and Co—O(CO<sub>3</sub>) = 1.914 (2)—1.963 (2) Å.

### Introduction

The synthesis, aquation, and redox properties of binuclear cobalt(III) complexes have been subjects of continuing interest during the last decade.<sup>1</sup> However, very few reports have appeared concerning binuclear complexes with carbonate either as a bridging or as a terminal group. The  $\mu$ -carbonato-bis[pentaamminecobalt(III)] ion is claimed to have been prepared in the pure state by several workers,<sup>2</sup> though recent attempts<sup>3</sup> have failed to reproduce any of these results. Baylis and Bailar<sup>4</sup> reported a binuclear diarsine cobalt(III) species with carbonate as a bridging ligand, but the structure of this complex has not been fully ascertained. Recently, we have become interested in the possibility of  $\mu$ -carbonato complex formation by the direct uptake of CO<sub>2</sub> by the OH groups of  $\mu$ -hydroxo-dicobalt(III) complexes. Reactions of a similar type involving various mononuclear cobalt(III)-hydroxo species are already well documented.<sup>5</sup> We have therefore begun by studying the reaction of  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] ion with carbonate in aqueous solution, a system somewhat comparable to that of our earlier study involving the  $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$  ion.<sup>6</sup> We have isolated the product of the reaction as a crystalline compound, determined its structure by X-ray diffraction, and examined some of its chemical properties, as reported in detail below.

### Experimental Section

**Preparation of Compounds. Preparation of  $\mu$ -Peroxo-bis[pentaamminecobalt(III)] Tetranitrate Dihydrate.** This compound was prepared from cobalt(II) nitrate and aqueous ammonia (15 M) as described in the literature;<sup>7</sup> yield 53.4%. The compound decomposes in water but is stable in 7 M ammonia. The visible spectrum of the complex is almost featureless.<sup>8</sup>

**Preparation of  $\mu$ -Amido- $\mu$ -superoxo-bis[tetraamminecobalt(III)] Tetranitrate.** A 45-g sample of freshly prepared  $\mu$ -peroxo salt was added in small portions to 500 mL of 15 M aqueous ammonia with continuous stirring. KOH (4.5 g) dissolved in 5 mL of water was added to the ammoniacal solution, and the resultant mixture was kept at  $35 \pm 2^\circ\text{C}$  for 1.5 h. The solution was then cooled to near 0 °C. The cooled solution was added dropwise to a cold mixture of 700 mL of concentrated nitric acid, 100 g of diammonium hexakis(nitrate)cerate(IV), and 1200 g of ice. Care should be taken at this stage

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Table I. Data for the X-ray Diffraction Study of  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$

(A) Crystal Data				
cryst system: monoclinic	$V = 1484.8$ (5) Å <sup>3</sup>			
space group: $P2_1/c$	$T = 23^\circ\text{C}$			
[ $C_{2h}^5$ ; No. 14]	$Z = 4$			
$a = 9.5572$ (15) Å <sup>a</sup>	mol wt 429.11			
$b = 15.8477$ (29) Å	$\rho(\text{obsd})^b = 1.864$ (13) g cm <sup>-3</sup>			
$c = 9.8036$ (20) Å	$\rho(\text{calcd}) = 1.919$ g cm <sup>-3</sup>			
$\beta = 90.305$ (14)°				
(B) Intensity Data				
radiation: Mo $K\alpha$ ( $\lambda$ 0.710 730 Å)				
monochromator: highly oriented graphite				
rflns measd: $+h, +k, \pm l$				
max $2\theta$ : 50.0°				
min $2\theta$ : 3.5°				
scan type: $\theta$ - $2\theta$				
scan speed: 4.0°/min				
scan range: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]^\circ$				
rflns collected: 3892 total, 3435 independent				
std rflns: 3 measd every 97 rflns; max devs from the mean were 3.7% for 217, 2.2% for 711, and 2.6% for 292; there was no significant decay				
abs coeff: $\mu = 22.96$ cm <sup>-1</sup>				
(C) Reflections Used for Empirical Absorption Correction <sup>c</sup>				
$h$	$k$	$l$	$2\theta$ , deg	$I_{\text{max}}/I_{\text{min}}$
0	1	3	12.72	1.25
0	1	5	21.00	1.24
2	3	6	27.70	1.31
2	1	7	30.76	1.28
2	3	8	35.70	1.31
2	1	9	39.15	1.27
0	6	11	49.66	1.30

<sup>a</sup> Based upon a least-squares fit to the setting angles of the unresolved Mo  $K\alpha$  components of 24 reflections of the forms  $\{217\}$ ,  $\{2,11,0\}$ ,  $\{711\}$ ,  $\{106\}$ ,  $\{702\}$ ,  $\{292\}$ , and  $\{631\}$ , all with  $2\theta = 25$ – $32^\circ$ . <sup>b</sup> Measured by flotation in *n*-butyl bromide/ethylene bromide. <sup>c</sup> For details of the experimental absorption correction, see: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* 1977, 16, 2655. Data averaging:  $R(I) = 1.45\%$  for 198 reflections with two or more contributors.

not to allow the temperature to rise above 0 °C. After complete addition, the mixture was allowed to remain in an ice-salt bath for 30 min and then left in the refrigerator overnight. The olive green precipitate was filtered and washed thoroughly with 2 M nitric acid. The green compound was used for the next step without further

**Table II.** Final Positional Parameters and Isotropic Thermal Parameters (with Esd's) for  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ 

atom	x	y	z	B, Å <sup>2</sup>
Co(1)	0.66609 (4)	0.41675 (3)	0.29878 (4)	
Co(2)	0.38850 (4)	0.47707 (3)	0.24753 (4)	
O(10)	0.54513 (25)	0.50689 (16)	0.35892 (23)	
N(1)	0.50545 (29)	0.38672 (19)	0.19155 (28)	
N(2)	0.77730 (34)	0.32291 (20)	0.22719 (32)	
N(3)	0.73499 (34)	0.48892 (21)	0.15060 (29)	
N(4)	0.59001 (35)	0.34770 (20)	0.44790 (28)	
N(5)	0.82102 (33)	0.45563 (23)	0.41903 (31)	
O(1)	0.29079 (23)	0.40968 (14)	0.37848 (20)	
O(2)	0.22138 (23)	0.42882 (15)	0.17009 (21)	
O(3)	0.08406 (26)	0.35377 (18)	0.31095 (26)	
C(1)	0.19201 (34)	0.39409 (21)	0.28786 (33)	
O(4)	0.43238 (22)	0.55656 (14)	0.10707 (20)	
O(5)	0.29422 (22)	0.58562 (14)	0.27635 (20)	
O(6)	0.31504 (27)	0.67923 (15)	0.10292 (24)	
C(2)	0.34628 (33)	0.61179 (20)	0.15885 (30)	
O(11)	0.6505 (6)	0.67353 (32)	0.3015 (5)	
O(22)	-0.02001 (32)	0.39146 (22)	0.01920 (31)	
O(33A)	0.0850 (10)	0.2831 (5)	0.5675 (7)	
O(33B)	-0.0145 (14)	0.2887 (6)	0.5375 (18)	
O(44)	0.6910 (6)	0.7089 (4)	0.0305 (6)	
O(55)	0.0021 (4)	0.58649 (25)	0.26757 (32)	
H(10)	0.570 (5)	0.5464 (28)	0.347 (5)	4.3 (13)
H(11)	0.479 (4)	0.3380 (27)	0.214 (4)	3.8 (10)
H(12)	0.5195 (35)	0.3897 (21)	0.1191 (35)	1.5 (7)
H(21)	0.760 (4)	0.2805 (25)	0.267 (4)	3.0 (9)
H(22)	0.759 (5)	0.3184 (28)	0.137 (5)	4.8 (11)
H(23)	0.869 (5)	0.3330 (27)	0.239 (4)	4.4 (11)
H(31)	0.764 (4)	0.5353 (26)	0.177 (4)	3.4 (10)
H(32)	0.805 (5)	0.4636 (31)	0.099 (5)	5.8 (12)
H(33)	0.666 (6)	0.508 (4)	0.093 (6)	7.9 (16)
H(41)	0.611 (4)	0.2915 (24)	0.444 (4)	2.8 (8)
H(42)	0.501 (5)	0.3527 (27)	0.449 (4)	4.3 (11)
H(43)	0.621 (5)	0.3630 (28)	0.528 (5)	4.6 (11)
H(51)	0.795 (5)	0.4958 (29)	0.469 (5)	4.5 (11)
H(52)	0.857 (5)	0.4180 (30)	0.462 (5)	4.8 (12)
H(53)	0.888 (5)	0.4859 (27)	0.381 (4)	4.1 (11)
H(1A)	0.684 (5)	0.6985 (28)	0.221 (5)	4.7 (11)
H(2A)	0.057 (5)	0.4149 (30)	0.066 (5)	5.8 (13)
H(2B)	-0.018 (5)	0.4041 (33)	-0.053 (5)	5.7 (14)
H(3A)	-0.020 (8)	0.234 (4)	0.553 (6)	8.6 (19)
H(3B)	0.042 (9)	0.309 (5)	0.486 (8)	11.1 (26)
H(5A)	0.069 (5)	0.581 (4)	0.276 (5)	5.7 (17)
H(5B)	-0.007 (5)	0.6365 (34)	0.308 (5)	5.9 (15)

purification. A small portion of this crude substance was purified according to the published procedure,<sup>7</sup> and the visible spectrum of this compound agreed well with that reported previously.<sup>9</sup>

**Preparation of  $\mu$ -Amido- $\mu$ -sulfato-bis[tetraamminecobalt(III)] Sulfate.** A 0.8-g sample of the superoxo complex was dissolved in 30 mL of 0.1 M nitric acid by heating at 60 °C. A vigorous stream of  $\text{SO}_2$  was then passed through the solution until a red precipitate started to appear. The solution was cooled to 0 °C in an ice-salt bath for 2 h. The red precipitate of  $\mu$ -amido- $\mu$ -sulfato complex was filtered, washed with ethanol and ether, and allowed to dry in a desiccator; yield 50%. The visible spectrum of the complex is in agreement with that in the literature.<sup>10</sup>

**Preparation of  $\mu$ -Amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] Tetrachloride Tetrahydrate.** A 5-g sample of the  $\mu$ -amido- $\mu$ -sulfato-cobalt(III) sulfate was added to 75 mL of concentrated hydrochloric acid. The mixture was stirred for 24 h. The red precipitate of  $\mu$ -amido- $\mu$ -chloro-bis[tetraamminecobalt(III)] chloride obtained was filtered and then crystallized from concentrated hydrochloric acid at 0 °C. To the red crystalline solid obtained was added distilled water (8 mL per gram of solid). The solution was filtered, and the filtrate was allowed to stand for 8 h. The dark red crystalline salt  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] chloride was obtained. This was filtered, washed with alcohol, and recrystallized from hot dilute acetic acid; yield 50% on the basis of  $\mu$ -amido- $\mu$ -chloro complex. The purity of the complex was checked by microanalysis.<sup>11</sup> Anal. Calcd for  $\text{Co}_2(\text{NH}_3)_8(\text{NH}_2)(\text{OH})\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ : H, 6.99; N, 25.15. Found: H, 6.87; N, 24.76. The purity was further checked by comparing the visible spectrum of the complex with that reported in the literature.<sup>12</sup>

**Preparation of  $\mu$ -Amido- $\mu$ -hydroxo-tetraamminebis(carbonato)-dicobalt(III) Pentahydrate.** A 0.2-g sample of  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] chloride was dissolved in 50 mL of 0.1 M sodium bicarbonate solution and heated at 40 °C for 3 h in a thermostated water bath. The solution was then kept in a refrigerator for 2 days when black needlelike crystals were separated. The crystals were filtered, washed thoroughly with water and alcohol, and dried in a desiccator; yield 80%. The purity of the complex was checked by microanalysis.<sup>11</sup> Anal. Calcd for  $\text{Co}_2(\text{NH}_3)_4(\text{CO}_3)_2(\text{NH}_2)(\text{OH}) \cdot 5\text{H}_2\text{O}$ : C, 5.59; H, 5.83; N, 16.31; Co, 27.50. Found: C, 5.53; H, 5.72; N, 16.63; Co, 27.20. The composition of this complex was established unambiguously by a full three-dimensional single-crystal X-ray diffraction study (vide infra).

**Preparation of  $\mu$ -Amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] Carbonate Hexahydrate.** When a concentrated solution of  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] chloride was made in water and solid sodium bicarbonate<sup>13</sup> was added in small portions with stirring, turbidity appeared. The solution was then cooled in an ice

**Table III.** Anisotropic Thermal Parameters<sup>a</sup> (Å<sup>2</sup>) for the Nonhydrogen Atoms in  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ 

atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Co(1)	1.524 (17)	1.909 (17)	1.146 (15)	0.087 (14)	0.067 (12)	-0.144 (12)
Co(2)	1.503 (17)	2.019 (18)	1.169 (15)	0.001 (14)	-0.039 (11)	-0.131 (13)
O(10)	1.89 (10)	2.19 (11)	1.98 (9)	0.06 (8)	-0.15 (7)	-0.41 (8)
N(1)	1.87 (11)	2.11 (12)	1.29 (10)	-0.18 (9)	0.08 (8)	-0.09 (9)
N(2)	2.34 (13)	2.39 (14)	2.08 (12)	0.03 (11)	0.43 (10)	0.05 (10)
N(3)	2.26 (13)	2.60 (14)	1.67 (11)	-0.21 (11)	0.12 (9)	-0.00 (9)
N(4)	2.69 (14)	2.20 (13)	1.64 (11)	0.29 (11)	0.36 (10)	0.04 (9)
N(5)	2.04 (12)	3.13 (15)	1.93 (11)	0.06 (12)	-0.15 (10)	-0.24 (11)
O(1)	1.98 (9)	2.82 (10)	1.55 (8)	-0.19 (8)	-0.08 (7)	0.08 (7)
O(2)	2.07 (9)	3.20 (11)	1.61 (8)	-0.43 (8)	-0.25 (7)	0.14 (8)
O(3)	2.53 (11)	4.84 (14)	3.28 (12)	-1.44 (10)	-0.29 (9)	0.74 (10)
C(1)	1.93 (14)	2.66 (15)	2.25 (13)	-0.38 (11)	0.04 (10)	-0.05 (11)
O(4)	2.10 (9)	2.32 (9)	1.38 (8)	0.25 (7)	0.16 (7)	-0.15 (7)
O(5)	1.99 (9)	2.54 (10)	1.47 (8)	0.20 (8)	0.26 (7)	-0.11 (7)
O(6)	3.67 (12)	2.12 (10)	2.85 (10)	0.36 (9)	0.23 (9)	0.24 (8)
C(2)	1.98 (13)	2.07 (13)	1.78 (12)	-0.23 (10)	-0.06 (10)	-0.30 (10)
O(11)	10.68 (35)	9.48 (31)	7.19 (27)	-3.44 (26)	0.65 (25)	-1.25 (24)
O(22)	3.08 (13)	6.29 (18)	2.13 (12)	-1.00 (12)	-0.19 (10)	0.24 (12)
O(33A)	7.2 (5)	4.5 (4)	3.88 (31)	-0.7 (4)	1.10 (32)	0.48 (24)
O(33B)	8.9 (7)	4.0 (4)	4.3 (4)	0.0 (5)	3.3 (5)	0.94 (31)
O(44)	12.9 (5)	11.3 (4)	12.6 (4)	-0.18 (33)	-2.16 (35)	-1.69 (32)
O(55)	2.31 (13)	5.59 (19)	3.20 (13)	-0.35 (13)	-0.06 (10)	-0.09 (12)

<sup>a</sup> The anisotropic thermal parameters enter the equation for the calculated structure factor in the form  $\exp[-0.25(h^2a^*B_{11} + \dots + 2hka^*b^*B_{12} + \dots)]$ .

**Table IV.** Intramolecular Distances (Å) with Esd's for  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ 

(A) Cobalt-(Bridging Ligand) Distances			
Co(1)-O(10)	1.932 (3)	Co(2)-O(10)	1.908 (2)
Co(1)-N(1)	1.916 (3)	Co(2)-N(1)	1.899 (3)
Co(1)···Co(2)	2.862 (1)		
(B) Cobalt-Ammine Distances			
Co(1)-N(2)	1.960 (3)	Co(1)-N(4)	1.968 (3)
Co(1)-N(3)	1.965 (3)	Co(1)-N(5)	1.986 (3)
(C) Cobalt-Carbonate Distances			
Co(2)-O(1)	1.917 (2)	Co(2)-O(4)	1.914 (2)
Co(2)-O(2)	1.923 (2)	Co(2)-O(5)	1.963 (2)
(D) Nitrogen-Hydrogen Distances			
N(1)-H(11)	0.84 (4)	N(1)-H(12)	0.72 (3)
N(2)-H(21)	0.80 (4)	N(4)-H(41)	0.91 (4)
N(2)-H(22)	0.90 (5)	N(4)-H(42)	0.85 (5)
N(2)-H(23)	0.89 (5)	N(4)-H(43)	0.87 (4)
N(3)-H(31)	0.83 (4)	N(5)-H(51)	0.84 (5)
N(3)-H(32)	0.93 (5)	N(5)-H(52)	0.81 (5)
N(3)-H(33)	0.91 (6)	N(5)-H(53)	0.88 (4)
(E) Carbon-Oxygen Distances			
C(1)-O(1)	1.316 (4)	C(2)-O(4)	1.306 (4)
C(1)-O(2)	1.311 (4)	C(2)-O(5)	1.324 (4)
C(1)-O(3)	1.236 (4)	C(2)-O(6)	1.237 (4)
(F) Oxygen-Hydrogen Distances			
O(10)-H(10)	0.68 (4)	O(33A)-H(3B)	0.98 (8)
O(11)-H(1A)	0.94 (5)	O(33B)-H(3A)	0.93 (7)
O(22)-H(2A)	0.94 (5)	O(33B)-H(3B)	0.81 (8)
O(22)-H(2B)	0.73 (5)	O(55)-H(5A)	0.66 (5)
O(33A)-H(3A)	1.00 (7)	O(55)-H(5B)	0.89 (5)

bath. The red shiny crystalline material obtained was filtered, washed with cold water and ethanol, and dried in a desiccator. Microanalysis of the compound confirms the structure to be  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraamminecobalt(III)] carbonate hexahydrate; yield 80%. Anal. Calcd for  $\text{Co}_2(\text{NH}_3)_8(\text{NH}_2)(\text{OH})(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$ : C, 4.61; H, 7.37; N, 25.22; Co, 22.60. Found: C, 4.57; H, 7.43; N, 24.01; Co, 22.45.

**Materials.** All the reagents used were of reagent grade. Distilled water, made from a Corning all-glass distillation unit, was used without further purification.  $\text{SO}_2$  gas (obtained from BDH Chemicals Ltd, Poole, England) and pure oxygen gas (obtained from JOAL, Jamaica) were used without any further treatment.

**Spectra.** The absorption spectra in the UV-visible region were obtained by use of a Unicam SP8000 recording spectrophotometer. (Extinction coefficients ( $\epsilon$ ) are reported in units of  $\text{M}^{-1} \text{cm}^{-1}$ .) The infrared spectra of the red carbonate salt and the black dicarbonate complex were measured with a Perkin-Elmer spectrometer, Model 735B, by using the KBr disk technique. The carbonate salt has a strong peak at  $1390 \text{ cm}^{-1}$  and a medium peak at  $855 \text{ cm}^{-1}$  which are comparable to the peaks at  $1445$  and  $885 \text{ cm}^{-1}$  obtained<sup>14</sup> for  $\text{K}_2\text{CO}_3$ . The  $\mu$ -amido- $\mu$ -hydroxo-tetraamminebis(carbonato)dicoalt(III) complex shows two strong peaks at  $1585$  and at  $1265 \text{ cm}^{-1}$ . These peaks are comparable to the strong peaks at  $1593 \text{ cm}^{-1}$  [ $\nu(\text{C}-\text{O}(11))$ ] and  $1265 \text{ cm}^{-1}$  [ $\nu(\text{C}-\text{O}(1)) + \delta(\text{O}(1)-\text{C}-\text{O}(11))$ ] obtained<sup>15</sup> for  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$ .

**Collection of X-ray Diffraction Data for  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ .** The crystal selected for the structural analysis was of approximately square cross section (0.20 mm in thickness) and 0.24 mm in length. It was mounted in a 0.2-mm-diameter glass capillary which was then sealed, set with beeswax into an aluminum pin, and mounted on an eucentric goniometer.

Preliminary precession photographs indicated  $2/m$  ( $C_{2h}$ ) Laue symmetry and revealed the systematic absences  $h0l$  for  $l = 2n + 1$  and  $0k0$  for  $k = 2n + 1$ . The centrosymmetric monoclinic space group  $P2_1/c$  [ $C_{2h}^5$ ; No. 14] is thereby uniquely defined. The crystal was transferred to a Syntex  $P2_1$  automated diffractometer and optically centered.

Accurate crystal alignment and determination of the orientation matrix and cell dimensions were carried out as described in detail previously.<sup>16</sup>

A series of  $\theta$ - $2\theta$  and  $\omega$  scans of reflections along the principal reciprocal axes were examined to check the crystal quality. The crystal was found to be satisfactory, and the collection of intensity data was carried out as described previously;<sup>16</sup> details are given in Table I.

Diffraction data were reduced to net intensities ( $I$ ) and their estimated standard deviations ( $\sigma_e(I)$ ). The ratio of time taken for the main scan to the total time for background measurement,  $\tau$ , was 1.50.

All data were corrected for the effects of absorption [ $\mu(\text{Mo K}\alpha) = 22.96 \text{ cm}^{-1}$ ] by an empirical method. Several close-to-axial reflections ( $\chi_0 = 69$ – $82^\circ$ ) distributed over the  $2\theta$  range used in data collection and each of fairly high intensity ( $I/\sigma(I) > 70$ ) were measured at  $10^\circ$  intervals of  $\psi$  (the diffraction vector) from  $0$  to  $350^\circ$ . Each reflection was used to define a normalized absorption curve vs.  $\phi$ , corrected for  $\omega$  and  $\chi$ . To derive the absorption correction, we interpolated the two curves bracketing the  $2\theta$  value of the reflection under consideration both in  $2\theta$  and in  $\phi$ . The reflections used are listed in Table I; they were all mutually consistent, with similar profiles and with maxima and minima at common values.

The check reflections were examined (no significant decay was detected) and deleted. The data were averaged according to  $2/m$  symmetry, and the intensities of the resulting 3435 independent reflections were corrected for Lorentz and polarization factors.

**Solution and Refinement of the Crystal Structure.** All calculations were performed by using a Syntex XTL structure determination system consisting of an in-house Data General Nova 1200 computer with 24K of 16-bit words, a Diablo disk unit of 1.2 million 16-bit words, and a locally modified version of the XTL conversational crystallographic program package.

The atomic scattering factors for neutral cobalt, oxygen, nitrogen, carbon and hydrogen used throughout the analysis were from the compilations of Cromer and Waber.<sup>17a</sup> Both real ( $\Delta f'$ ) and imaginary ( $\Delta f''$ ) components of anomalous dispersion were included for all nonhydrogen atoms by using the values of Cromer and Liberman.<sup>17b</sup>

The function minimized during least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ . The weights used were obtained from counting statistics, modified by an "ignorance factor",  $p$ , set at a value of 0.010.

The positions of the cobalt atoms were found from an unsharpened Patterson synthesis. Full-matrix least-squares refinement of the scale factor and the positional and isotropic thermal parameters for the two cobalt atoms using only those data with  $(\sin \theta)/\lambda < 0.54$  and  $|F_o| > \sigma(F_o)$  (a "cut-down" data set of 1871 reflections) led to  $R_F = 40.1\%$  and  $R_{wF} = 46.2\%$ . A difference Fourier synthesis at this point, with the same data restrictions, revealed the positions of the two carbonate ligands, the nitrogen atoms of the four terminal amines, and the two bridging atoms (which initially were treated as nitrogen atoms). Full-matrix least-squares refinement of positional and isotropic thermal parameters gave  $R_F = 17.1\%$ ,  $R_{wF} = 21.7\%$ , and  $\text{GOF} = 10.06$ . A difference Fourier synthesis based upon the restricted data set revealed five maxima of peak height  $8.60$ – $3.97 \text{ e } \text{Å}^{-3}$  at distances of  $< 3.0 \text{ Å}$  to atoms in the molecule. These maxima correspond to the positions of the oxygen atoms of five hydrogen-bonded water molecules and were included in our model.

From careful inspection of isotropic thermal parameters we were able to reassign one of the atoms bridging the cobalt atoms as an oxygen (part of a bridging hydroxide).

Refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms using all data resulted in  $R_F = 5.7\%$ ,  $R_{wF} = 6.3\%$ , and  $\text{GOF} = 2.99$ .

A difference Fourier synthesis based now upon all data revealed all the hydrogen atoms present in the  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2$  molecule. Continued refinement including the positional and isotropic thermal parameters of these hydrogen atoms gave  $R_F = 5.0\%$ ,  $R_{wF} = 4.9\%$ , and  $\text{GOF} = 2.32$ .

At this point, we attempted to locate unambiguously all hydrogen atoms associated with the waters of crystallization. All but three were found on a difference Fourier synthesis using all data. From this difference Fourier synthesis we also found that the oxygen atom of one of the water molecules is disordered while its hydrogens apparently are not.

Least-squares refinement of all nonhydrogen positional and anisotropic thermal parameters and of the known hydrogen positional and isotropic thermal parameters resulted in  $R_F = 4.5\%$ ,  $R_{wF} = 4.0\%$ , and  $\text{GOF} = 1.94$ .

Careful comparison of observed and calculated structure factor amplitudes indicated that a correction for secondary extinction was necessary. The value for the secondary extinction parameter ( $k$ ) used was  $2.537 \times 10^{-8}$ .  $F_{o,\text{cor}}$ , the corrected observed structure factor, and  $\sigma(F_{o,\text{cor}})$  are given by eq 1 and 2, respectively.

$$F_{o,\text{cor}} = F_o(1.0 + kI) \quad (1)$$

Table V. Interatomic Angles (deg) with Esd's, for  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ 

(A) Angles Involving the Bridging Ligands			
Co(1)-N(1)-Co(2)	97.19 (13)	H(11)-N(1)-H(12)	112 (4)
N(1)-Co(1)··Co(2)	41.18 (9)	Co(1)-O(10)-Co(2)	96.38 (11)
N(1)-Co(2)··Co(1)	41.63 (9)	O(10)-Co(1)··Co(2)	41.49 (7)
N(1)-Co(2)-O(10)	83.74 (11)	O(10)-Co(2)··Co(1)	42.13 (7)
N(1)-Co(1)-N(2)	92.84 (13)	O(10)-Co(1)-N(1)	82.65 (11)
N(1)-Co(1)-N(3)	90.55 (13)	O(10)-Co(1)-N(2)	175.46 (12)
N(1)-Co(1)-N(4)	88.36 (12)	O(10)-Co(1)-N(3)	89.93 (12)
N(1)-Co(1)-N(5)	174.57 (13)	O(10)-Co(1)-N(4)	87.73 (12)
N(1)-Co(2)-O(1)	93.62 (11)	O(10)-Co(1)-N(5)	92.00 (12)
N(1)-Co(2)-O(2)	94.30 (11)	O(10)-Co(2)-O(1)	97.95 (10)
N(1)-Co(2)-O(4)	99.01 (11)	O(10)-Co(2)-O(2)	166.39 (10)
N(1)-Co(2)-O(5)	166.78 (11)	O(10)-Co(2)-O(4)	94.27 (10)
Co(1)-N(1)-H(11)	109 (3)	O(10)-Co(2)-O(5)	93.43 (10)
Co(1)-N(1)-H(12)	112 (3)	Co(1)-O(10)-H(10)	115 (4)
Co(2)-N(1)-H(11)	116 (3)	Co(2)-O(10)-H(10)	114 (4)
Co(2)-N(1)-H(12)	110 (3)		
(B) Cobalt-Cobalt-Ligand Angles			
Co(2)··Co(1)-N(2)	133.99 (10)	Co(1)··Co(2)-O(1)	98.68 (7)
Co(2)··Co(1)-N(3)	89.42 (9)	Co(1)··Co(2)-O(2)	134.72 (7)
Co(2)··Co(1)-N(4)	88.30 (9)	Co(1)··Co(2)-O(4)	98.03 (6)
Co(2)··Co(1)-N(5)	133.49 (10)	Co(1)··Co(2)-O(5)	133.88 (6)
(C) Ligand-Cobalt-Ligand Angles			
N(2)-Co(1)-N(3)	89.56 (13)	O(1)-Co(2)-O(2)	68.67 (9)
N(2)-Co(1)-N(4)	92.71 (13)	O(1)-Co(2)-O(4)	163.29 (9)
N(2)-Co(1)-N(5)	92.52 (14)	O(1)-Co(2)-O(5)	99.57 (9)
N(3)-Co(1)-N(4)	177.52 (13)	O(4)-Co(2)-O(5)	68.24 (9)
N(3)-Co(1)-N(5)	90.37 (13)	O(4)-Co(2)-O(2)	99.34 (9)
N(4)-Co(1)-N(5)	90.51 (13)	O(5)-Co(2)-O(2)	91.39 (9)
(D) Other Angles Involving the Carbonate Ligands			
O(1)-C(1)-O(2)	111.07 (27)	O(4)-C(2)-O(5)	111.63 (26)
O(1)-C(1)-O(3)	124.75 (30)	O(4)-C(2)-O(6)	123.91 (29)
O(2)-C(1)-O(3)	124.16 (30)	O(5)-C(2)-O(6)	124.44 (28)
Co(2)-O(1)-C(1)	90.16 (18)	Co(2)-O(4)-C(2)	91.18 (18)
Co(2)-O(2)-C(1)	90.03 (19)	Co(2)-O(5)-C(2)	88.54 (17)
(E) Other Angles Involving the Ammine Ligands			
Co(1)-N(2)-H(21)	111 (3)	H(21)-N(2)-H(22)	112 (4)
Co(1)-N(2)-H(22)	108 (3)	H(21)-N(2)-H(23)	107 (4)
Co(1)-N(2)-H(23)	111 (3)	H(22)-N(2)-H(23)	109 (4)
Co(1)-N(3)-H(31)	113 (3)	H(31)-N(3)-H(32)	108 (4)
Co(1)-N(3)-H(32)	113 (3)	H(31)-N(3)-H(33)	98 (5)
Co(1)-N(3)-H(33)	113 (4)	H(32)-N(3)-H(33)	110 (5)
Co(1)-N(4)-H(41)	116 (2)	H(41)-N(4)-H(42)	108 (4)
Co(1)-N(4)-H(42)	109 (3)	H(41)-N(4)-H(43)	104 (4)
Co(1)-N(4)-H(43)	113 (3)	H(42)-N(4)-H(43)	108 (4)
Co(1)-N(5)-H(51)	111 (3)	H(51)-N(5)-H(52)	113 (5)
Co(1)-N(5)-H(52)	113 (3)	H(51)-N(5)-H(53)	93 (4)
Co(1)-N(5)-H(53)	117 (3)	H(52)-N(5)-H(53)	108 (4)
(F) Hydrogen-Oxygen-Hydrogen Angles			
H(2A)-O(22)-H(2B)	110 (5)	H(3A)-O(33B)-H(3B)	103 (7)
H(3A)-O(33A)-H(3B)	87 (6)	H(5A)-O(55)-H(5B)	100 (6)

$$\sigma(F_{o,\text{cor}}) = \sigma(F_o)[1.0 + kI] \quad (2)$$

Continued refinement led to convergence with  $R_F = 4.4\%$ ,  $R_{wF} = 3.8\%$ , and  $\text{GOF} = 1.84$  for all 3435 data; those data with  $I < \sigma(I)$  were given zero weight in the refinement process.

A final difference Fourier synthesis based on all data had a peak of height  $0.78 \text{ e } \text{\AA}^{-3}$  close to a  $\text{H}_2\text{O}$  molecule; all other peaks were  $< 0.52 \text{ e } \text{\AA}^{-3}$  in height.

The average value of  $\sum w(|F_o| - |F_c|)^2$  showed no significant variations as a function of  $|F_o|$ ,  $(\sin \theta)/\lambda$ , identity or parity of Miller indices, or sequence number. The weighting scheme is therefore acceptable. The final NO:NV ratio was 3435:287 or 11.97:1.

The final positional and thermal parameters are listed in Tables II and III.

## Results and Discussion

**Molecular and Crystal Structure.** Interatomic distances and angles are collected in Tables IV and V; important least-squares planes are given in Table VI. The molecular geometry and atomic labeling scheme for the  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2$  molecule are shown in Figure 1.

Each of the cobalt(III) ions is in an approximately octahedral environment. The dinuclear cluster has some zwitterionic character since four neutral  $\text{NH}_3$  ligands are associated with Co(1), while two dinegatively charged  $\text{CO}_3^{2-}$  ligands chelate to Co(2). There is a slight asymmetry in the  $(\mu\text{-NH}_2)(\mu\text{-OH})$  bridge, such that the bridging ligands are slightly further from Co(1) than from Co(2): i.e.,  $\text{Co(1)-N(1)} = 1.916(3) \text{ \AA}$  vs.  $\text{Co(2)-N(1)} = 1.899(3) \text{ \AA}$  ( $\Delta = 4.0\sigma$ ) and  $\text{Co(1)-O(10)} = 1.932(3) \text{ \AA}$  vs.  $\text{Co(2)-O(10)} = 1.908(2) \text{ \AA}$  ( $\Delta = 6.7\sigma$ ).

The mutually trans axial ammine ligands, centered on N(3) and N(4) have equivalent cobalt-nitrogen bond lengths,  $\text{Co(1)-N(3)} = 1.965(3) \text{ \AA}$  and  $\text{Co(1)-N(4)} = 1.968(3) \text{ \AA}$ ; the equatorial cobalt-ammine linkages appear to be inequivalent, with that trans to the bridging amide ligand being slightly longer than that trans to the bridging hydroxide ligand—i.e.,  $\text{Co(1)-N(5)} = 1.986(3) \text{ \AA}$  vs.  $\text{Co(1)-N(2)} = 1.960(3) \text{ \AA}$  ( $\Delta = 6.0\sigma$ ). The intermetallic distance ( $\text{Co(1)··Co(2)} = 2.862(1) \text{ \AA}$ ) and angles at the bridging ligands [ $\text{Co(1)-N(1)-Co(2)} = 97.19(13)^\circ$  and  $\text{Co(1)-O(10)-Co(2)}$

**Table VI.** Important Least-Squares Planes for  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}^{a,b}$ 

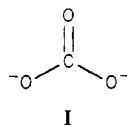
atom	dev, Å	atom	dev, Å
Plane I: $0.3472X + 0.5725Y - 0.7428Z = 3.7991$			
Co(1)*	0.0113 (4)	H(12)	0.59 (3)
Co(2)*	0.0115 (4)	N(2)	0.052 (3)
O(10)*	-0.0113 (24)	N(5)	0.000 (3)
N(1)*	-0.0115 (28)	O(2)	-0.415 (2)
H(10)	0.52 (5)	O(5)	0.473 (2)
H(11)	-0.70 (4)		
Plane II: $0.4694X - 0.8392Y - 0.2745Z = -5.1693$			
C(1)*	0.008 (3)	Co(2)	-0.1045 (4)
O(1)*	-0.002 (2)	O(10)	-0.101 (2)
O(2)*	-0.002 (2)	N(1)	1.774 (3)
O(3)*	-0.003 (3)		
Plane III: $-0.7551X - 0.4453Y - 0.4812Z = -7.5514$			
C(2)*	-0.008 (3)	Co(2)	0.2231 (4)
O(4)*	0.003 (2)	O(10)	-1.639 (2)
O(5)*	0.003 (2)	N(1)	0.279 (3)
O(6)*	0.003 (2)		

<sup>a</sup> Equations of planes are expressed in the orthonormal coordinates  $X$ ,  $Y$ , and  $Z$  where  $X = xa + zc \cos \beta$ ,  $Y = yb$ , and  $Z = zc \sin \beta$ . <sup>b</sup> Atoms marked with an asterisk were used in calculating the plane under consideration.

$= 96.38 (11)^\circ$ ] indicate that there is no bonding cobalt-cobalt interaction. (The average cobalt-ammine distance of 1.970 Å and the covalent radius of 0.70 Å for nitrogen suggest a covalent radius of 1.27 Å for Co(III) in the present complex; a  $\text{Co}^{\text{III}}\text{-Co}^{\text{III}}$  single bond would thus be  $\sim 2.54$  Å in length.)

The chelating carbonate ligands cause some perturbation in the octahedral environment about Co(2), the "bite angles" being  $\text{O}(1)\text{-Co}(2)\text{-O}(2) = 68.67 (9)^\circ$  and  $\text{O}(4)\text{-Co}(2)\text{-O}(5) = 68.24 (9)^\circ$ . The individual  $\text{Co-O}(\text{CO}_3)$  distances range from 1.914 (2) to 1.963 (2) Å. The mutually trans (axial) linkages are equivalent ( $\text{Co}(2)\text{-O}(1) = 1.917 (2)$  Å and  $\text{Co}(2)\text{-O}(4) = 1.914 (2)$  Å) while the equatorial linkages are not. Once again, as with ammine ligands (vide supra), the linkage trans to the bridging amide ligand is longer than that trans to the bridging hydroxide ligand [ $\text{Co}(2)\text{-O}(5) = 1.963 (2)$  Å vs.  $\text{Co}(2)\text{-O}(2) = 1.923 (2)$  Å;  $\Delta = 16.4\sigma$ ].

The carbonate ligands each take up a geometry indicative of a fixed valence bond structure (see I). Those oxygen atoms

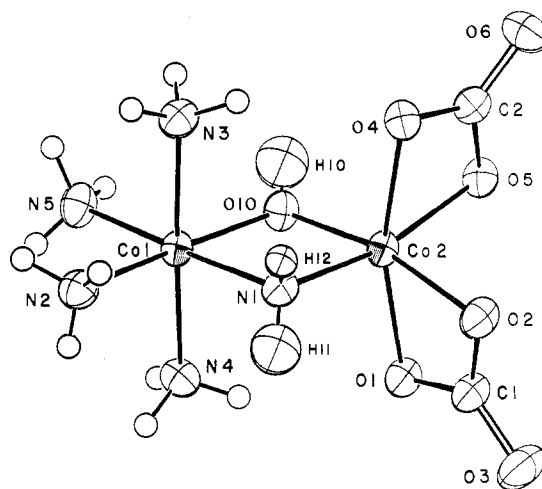


not involved in bonding to the cobalt atoms participate in

**Table VII.** Distances and Angles Involving Hydrogen Bonding<sup>a</sup>

atoms	trans	dist, Å	atoms	angle, deg
O(11)···O(10)	1 0 0 0	2.883 (6)	O(11)···H(10)-O(10)	179 (5)
O(11)···O(44)	1 0 0 0	2.744 (8)	O(11)-H(1A)···O(44)	152 (4)
O(11)···O(33A)	3 1 1 1	2.912 (11)		
O(22)···N(3)	1 -1 0 0	3.092 (4)	O(22)···H(32)-N(3)	168 (4)
O(22)···O(2)	1 0 0 0	2.797 (4)	O(22)-H(2A)···O(2)	163 (4)
O(22)···O(55)	3 0 1 0	2.839 (4)	O(22)-H(2B)···O(55)	168 (5)
O(33A)···O(22)	4 0 1 1	2.980 (9)	O(33A)-H(3A)···O(22)	152 (6)
O(33A)···O(3)	1 0 0 0	2.753 (8)	O(33A)-H(3B)···O(3)	143 (7)
O(33B)···O(22)	4 0 1 1	2.860 (10)	O(33B)-H(3A)···O(22)	143 (6)
O(33B)···O(3)	1 0 0 0	2.628 (11)	O(33B)-H(3B)···O(3)	149 (8)
O(44)···O(11)	4 0 2 0	2.942 (8)		
O(44)···O(33A)	2 1 0 0	2.629 (11)		
O(55)···N(5)	1 -1 0 0	3.086 (5)	O(55)···H(53)-N(5)	163 (4)
O(55)···O(5)	1 0 0 0	2.793 (4)	O(55)-H(5A)···O(5)	168 (6)
O(55)···O(33A)	3 0 1 1	2.756 (9)	O(55)-H(5B)···O(33A)	156 (5)
O(55)···O(33B)	3 0 1 1	2.753 (11)	O(55)-H(5B)···O(33B)	152 (5)

<sup>a</sup> The transformation of the second atom is given by a four-digit code. The first represents the equipoint (see below) while the second through fourth represent the addition (+1) or subtraction (-1) of unit cell vectors  $a$ ,  $b$ , and  $c$ . Transformation code: (1)  $x, y, z$ ; (2)  $-x, 1/2 + y, 1/2 - z$ ; (3)  $-x, -y, -z$ ; (4)  $x, -1/2 - y, -1/2 + z$ .

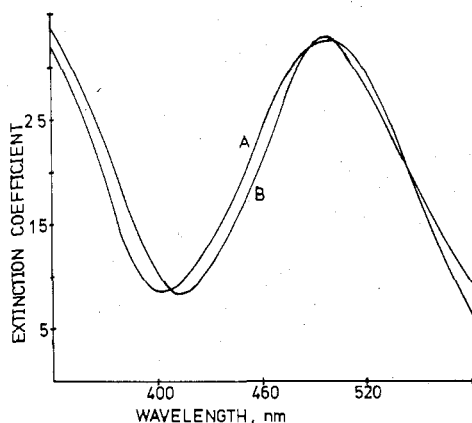
**Figure 1.** Labeling of atoms in the  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2$  ion (ORTEP-II diagram; 50% ellipsoids for nonhydrogen atoms).

carbon-oxygen double bonds [viz.,  $\text{C}(1)\text{-O}(3) = 1.236 (4)$  Å and  $\text{C}(2)\text{-O}(6) = 1.237 (4)$  Å], while the four metal-bonded oxygens are involved in longer carbon-oxygen bonds [ $\text{C}(1)\text{-O}(1) = 1.316 (4)$  Å,  $\text{C}(1)\text{-O}(2) = 1.311 (4)$  Å,  $\text{C}(2)\text{-O}(4) = 1.306 (4)$  Å,  $\text{C}(2)\text{-O}(5) = 1.324 (4)$  Å; average  $1.314 \pm 0.008$  Å]. The carbonate ligands are each close to planar, but in each case the carbon atom is displaced very slightly from the plane defined by the surrounding oxygen atoms—by 0.010 Å for C(1) and by 0.011 Å for C(2) (see Table VI).

Finally we note that all hydrogen atoms in the  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2$  ion were located and refined, leaving no ambiguity as to the relative identity of the bridging ligands. Dimensions involving the hydrogen atoms are included in Tables IV and V.

**Hydrogen Bonding in the Crystal.** There is an extensive hydrogen bonding scheme within the crystal. Relevant dimensions are given in Table VII; the disorder of one water molecule into two sites (centered on O(33A) and O(33B)) and the resulting bifurcation of the hydrogen bonding, coupled with our failure to locate all hydrogen atoms in the water molecules, make impossible a detailed discussion of this feature.

**Chemical Properties.** The black crystalline solid  $\mu$ -amido- $\mu$ -hydroxo-tetraamminebis(carbonato)dicobalt(III) pentahydrate is insoluble at room temperature in water, dimethyl sulfoxide, dimethylformamide, ethanol, methanol, acetonitrile, benzene, and toluene. In water at 80 °C, it decomposes to yield a dark brown solution. When the solid is heated with aqueous acid, it aquates rapidly, liberating  $\text{CO}_2$



**Figure 2.** Absorption spectra for (A)  $(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Co}(\mu\text{-NH}_2)\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_3$  and (B)  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{H}_2\text{O})_4$  in water. The extinction coefficient is given in units of  $\text{M}^{-1} \text{cm}^{-1}$ .

and producing a solution of  $\mu$ -amido- $\mu$ -hydroxo-tetraamminetetraaquadicobalt(III) ion. The spectrum of this tetraaquo ion is very similar to that of the final product of the hydrolysis of  $[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{NH}_3)_4]^{4+}$  ion reported by Taylor and Sykes<sup>19</sup> (see Figure 2). The surprising feature of our study is that the bridging hydroxide group exhibits no reactivity toward the  $\text{CO}_2$  present in the reaction mixture. Apparently, the double coordination of this OH entity greatly decreases its nucleophilicity toward carbon dioxide. This is in contrast to the terminal Co-OH grouping in mononuclear cobalt(III) species and to the free aqueous  $\text{OH}^-$  ion itself. The reaction observed is the unexpectedly effective substitution of  $\text{CO}_3^{2-}$  for  $\text{NH}_3$ , which apparently is facilitated by the adjacent  $\mu\text{-OH}$  species. It has already been noted<sup>19</sup> that the  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraammincobalt(III)] ion loses  $\text{NH}_3$  during acid hydrolysis, in spite of the fact that ammine ligands normally are extremely inert when coordinated to cobalt(III).<sup>20</sup> A similar type of labilization may account for the displacement of ammonia by carbonate in our system. However, the rate of substitution of  $\text{CO}_3^{2-}$  for  $\text{NH}_3$  is much greater than that of hydrolysis in acidic media,<sup>21</sup> which suggests that either  $\text{CO}_2$  or  $\text{CO}_3^{2-}$  catalyzes the release of ammonia. It should also be noted that once one carbonate ligand enters the cobalt(III) coordination sphere, it labilizes the adjacent  $\text{NH}_3$  ligand, enabling the entry of a second  $\text{CO}_3^{2-}$  ion and the chelation of both carbonates. This contrasts sharply with the previous observation<sup>19</sup> that elimination of more than one  $\text{NH}_3$  ligand from the same cobalt(III) center is always difficult, at least in acidic solution. Finally, it should be noted that a bridging hydroxo group in doubly bridged cobalt(III) complexes labilizes the second bridge if it is a hydroxo bridge<sup>23</sup> but not if it is an amido group. For example, in carbonate solution, the complete cleavage of both hydroxo bridges occurs in di- $\mu$ -hydroxo-dicobalt(III) complexes with ammine or ethylenediamine as terminal ligands.<sup>22</sup> The products of these reactions are 2 mol of the corresponding chelated (carbonato)tetraammine- or (carbonato)bis(ethylenediamine)cobalt(III) complex.

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**Registry No.**  $(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ , 70576-37-3;  $[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{NH}_3)_4](\text{CO}_3)_2$ , 70562-04-8;  $[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{NH}_3)_4]\text{Cl}_4$ , 15008-23-8;  $\mu$ -amido- $\mu$ -sulfato-bis[tetraammincobalt(III)] sulfate, 15772-01-7;  $\mu$ -amido- $\mu$ -superoxo-bis[tetraammincobalt(III)] tetranitrate, 12139-90-1;  $\mu$ -peroxo-bis[pentaammincobalt(III)] tetranitrate, 16632-71-6;  $[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{H}_2\text{O})_4]^{4+}$ , 70562-05-9.

**Supplementary Material Available:** Data processing formulas and a listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

## References and Notes

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- (9) The extinction coefficients of  $\mu$ -amido- $\mu$ -superoxo-bis[tetraammincobalt(III)] ion are 308 and 382 at 700 and 475 nm, respectively (cf. the extinction coefficients of 306 and 368 at these wavelengths reported by: Stevenson, M. B.; Sykes, A. G. *J. Chem. Soc. A* **1969**, 2979.)
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- (12) The extinction coefficient of the  $\mu$ -amido- $\mu$ -hydroxo-bis[tetraammincobalt(III)] chloride is 153 at  $\lambda_{\text{max}}$  522 nm (cf.  $\lambda_{\text{max}}$  520 ( $\epsilon$  149) in ref 16).
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